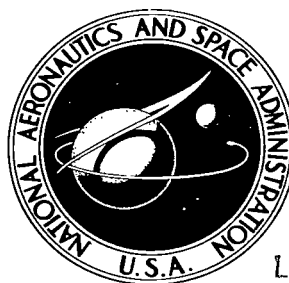


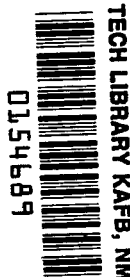
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*by William A. Gordon*

*Lewis Research Center*

*Cleveland, Ohio*



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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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# USE OF TEMPERATURE BUFFERED ARGON ARC IN SPECTROGRAPHIC TRACE ANALYSIS

by William A. Gordon

Lewis Research Center

## SUMMARY

A new and widely applicable procedure is described for improving the lower limits of detection of trace elements by emission spectroscopy. A special gas-tight chamber was used that permits the arcing of specimens in a static atmosphere of argon at pressures from 100 to 7500 torr. Observations of the physical features of the argon arc in this pressure range are reported.

The criterion used to establish the optimum arcing conditions was the measurement of the line-to-background intensity ratios. Experimental parameters were studied to determine conditions for maximizing the elemental line intensities and minimizing the background radiation. The sensitive neutral atom lines are enhanced in this system, and the characteristic ion spectra of the argon arc are suppressed by vaporizing a few milligrams of certain metal salts into the discharge with the sample. All of the common "carrier" salts produce this effect, which is believed to be caused by a lowering of the effective excitation temperature of the arc. Although the background intensity decreases linearly down to about 100 torr, the line-to-background ratio was found to be a maximum for most elements at about 350 torr.

This system for trace analysis has been applied to the determination of trace elements in dilute solutions. The absolute sensitivities attained are of the order of  $10^{-8}$  to  $10^{-10}$  gram, which compare favorably to the sensitivities reported when using hollow cathode excitation. Unlike the hollow cathode, however, this system can be applied to the determination of trace elements in refractory and volatile samples with equal facility.

## INTRODUCTION

The requirements for the analysis of purified materials often exceed the capabilities of direct spectrographic analysis because of inadequate detectability of the technique as presently practiced.

A considerable effort is directed toward the goal of extending analytical measurements. This is shown by a worldwide survey in which it is stated that "nearly half the new methods of analysis are concerned with progressively smaller concentrations of substances" (ref. 1).

In emission spectroscopy, attempts to extend detection limits have been primarily concerned with improving sources of radiation. Gains in sensitivity of an order of magnitude or more are often achieved with relatively little effort by changing conditions at the source of excitation. In contrast, instrumental effects such as stray light, dispersion, and resolution may affect the limits of detection, but improvements of these factors in instrumentation are done only with considerable effort and expense.

It has long been recognized that the blend of oxygen and nitrogen peculiar to air is not always best for problems of analysis in spectrochemistry. The popularity of air as a discharge medium arises primarily from the convenience of the approach. The benefits derived from conducting arc excitation in gases other than air have been described by Adelstein and Vallee (ref. 2) and by Vallee and Peattie (ref. 3). These authors reported that occasionally lower limits of detection were achieved using helium and argon as the arcing atmosphere. They surmised that this improvement was due to the prolongation of sample vaporization. Flowing gas systems of argon-nitrogen mixtures (ref. 4) and pure argon (ref. 5) have been used for the determination of trace elements in high purity nickel and silicon carbide. These authors also attribute the high sensitivity to the prolonged time required for the impurity elements to be completely evolved under these conditions.

All of the aforementioned procedures employ flowing gas systems, and the data reported therefore are at atmospheric or slightly positive pressures. Some emission sources, however, that have characteristically low background, such as the hollow cathode and some discharge tubes, are operated at pressures less than atmospheric and might appear to produce favorable line-to-background ratios for trace analysis due to reduction of background. Although these sources are sometimes useful for special problems in trace analysis, their use is limited for materials having moderately high boiling points. The low power at which these sources customarily operate limits their utility to only the more volatile samples.

The effects of gas pressure on line-to-background ratios in the direct-current arc at currents commonly used in analytical spectroscopy are little known. In reference 6 the effects of pressure on arc excitation at pressures from 760 through 5300 torr in carbon dioxide are reported. Increases were noted in the integrated line intensities of copper and lithium, and the enhancement was attributed to a decrease in diffusion coefficients for atoms in the arc column at higher pressures. Zakharov (ref. 7) measured the atomic concentrations of sodium, lithium, barium, calcium, and strontium in an arc discharge in an atmosphere of air at pressures from 10 to 760 torr. The data showed that in general the atom population in the discharge increases at higher pressures for sodium,

lithium, and calcium. Strontium exhibited a peak at 190 torr, and barium remained essentially unchanged. For various sodium salts the atomic concentration in the discharge was greater for compounds with smaller heats of formation. From the data presented it was not possible to determine the relative importance of excitation effects and other factors such as diffusion. Alexander operated a 5-ampere direct-current arc at pressures from 100 to 2300 torr and reported<sup>1</sup> enhancements in line emission for many elements at higher pressures. Atmospheres of helium, neon, argon, krypton, and nitrogen (N<sub>2</sub>) were compared, and in virtually all cases the relative line intensities were enhanced as the discharge pressure was increased. The author postulated that the line enhancements under these conditions arise from an excitation phenomenon, such as a more probable transfer of energy to the sample atoms by collisions with gas atoms. The samples used in this work were aqueous solutions of metallic salts dried on graphite electrodes.

In these investigations it was not always apparent how the reported intensity parameter could be related to analytical sensitivity. For example, the data were on occasion reported in terms of time-integrated line intensities as well as net line intensities and line-to-background ratios. The evaluation of this data for use in trace analysis must be made with a knowledge of the limiting conditions encountered in a given system. The two basic situations in spectrochemical methods that define limiting conditions in trace analysis are (1) when there is insufficient light at the detector to cause a measurable response (i. e., image on the photographic plate), and (2) when the line emission cannot be observed above background. These concepts are customarily termed absolute and relative sensitivity, respectively. Absolute sensitivity may be improved by amplification using such procedures as longer exposures (when samples permit), faster photographic emulsions, more efficient focusing of the source light, and a more sensitive detector (photomultiplier). Thus, Alexander's procedure improves absolute limits of detection by arcing samples in pure argon at pressures above atmospheric. Under these conditions the constricted positive column of a direct-current arc becomes brighter, and more light, both line emission and background, is transmitted to the photographic plate.

Amplification alone will not improve relative limits of detection since in the usual sense amplification does not discriminate between line emission and the masking effect of the background. A criterion that has been widely used in establishing relative limits of detection is the measurement of the line-to-background intensity ratio. This criterion was proposed originally for photographic detection and is valid in most cases using conventional photographic photometry. Several authors (refs. 8 to 10) define detection limits in terms of the variability of the line-to-background ratios since in practice neither

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<sup>1</sup>Oral presentation, "Controlled Atmosphere Arc Spectroscopy," at Tenth International Conference on Spectroscopy, 1962, College Park, Md.

the line nor the background intensities are constant. While the latter is a more rigorous method for establishing a detection criterion, the line-to-background intensity ratio provides a more convenient measurement of relative detection limits when comparing various sets of experimental conditions. Line-to-background ratios reported in this work were calculated as follows:

$$\frac{I \text{ line}}{I \text{ background}} = \frac{I(\text{line} + \text{background})}{I \text{ background}} - 1$$

In photographic detection it is generally desired to produce line radiation at least 30 percent more intense than the accompanying background (i. e., a line-to-background ratio of 0.3) so that the photometric error is not unduly large. Additional increases in the ratio at a given concentration, however, will not necessarily result in analytical methods with lower limits of determination. A realistic criterion for the limit of determination, in contrast to limit of detection, of an analytical method must include a statement reflecting the statistical confidence in the concentrational measurement, as pointed out in reference 8. For example, the limit of determination may be stated in terms of the precision of measurement such as the standard deviation or a multiple thereof. Since the precision with which analytical measurements are made is dependent on other factors in addition to line-to-background ratios, the ratio is not necessarily fundamental in establishing the limit of determination. The results reported in this investigation are therefore concerned with and most useful for those determinations that are line-to-background limited; that is, the line intensity is not observed over the intensity of the background light. In such cases any procedure that improves the line-to-background intensity ratio will improve the capability to measure lower concentrations.

In the present work, conditions were established for improving line-to-background ratios in a direct-current arc operated at pressures reduced from atmospheric. The effect of argon pressure on line-to-background intensity ratios is described. The use of a carrier salt such as silver chloride lowers the effective excitation temperature of the arc permitting the use of the sensitive neutral atom lines of the common elements.

## APPARATUS

The operation of the arc at reduced pressure requires a vacuum-tight chamber. The apparatus used in this work was similar to the chamber described in reference 11 for the determination of gases in metals. Figure 1 shows the essential features of the device. Basically, the chamber consists of an upper and a lower stainless-steel plate with provisions for water cooling. Electrical insulation and vacuum sealing are provided by a

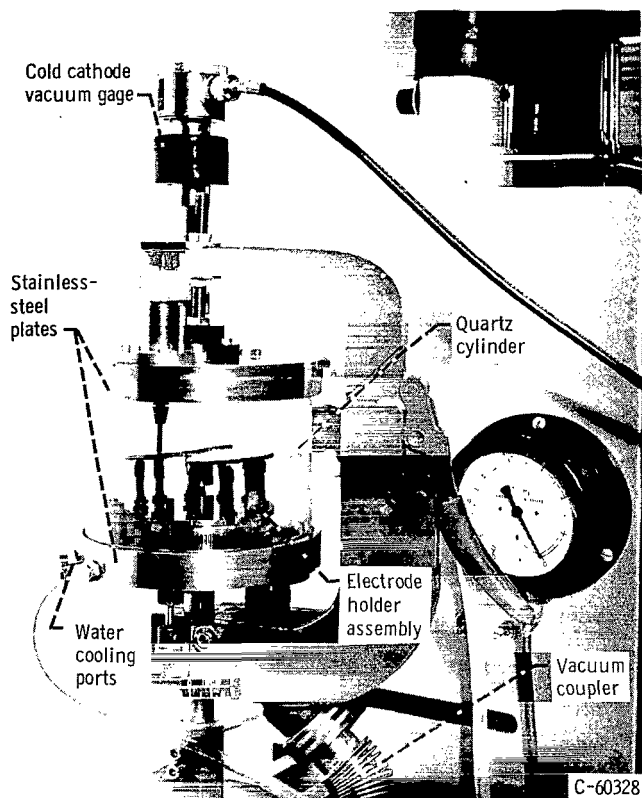


Figure 1. - Controlled atmosphere chamber.

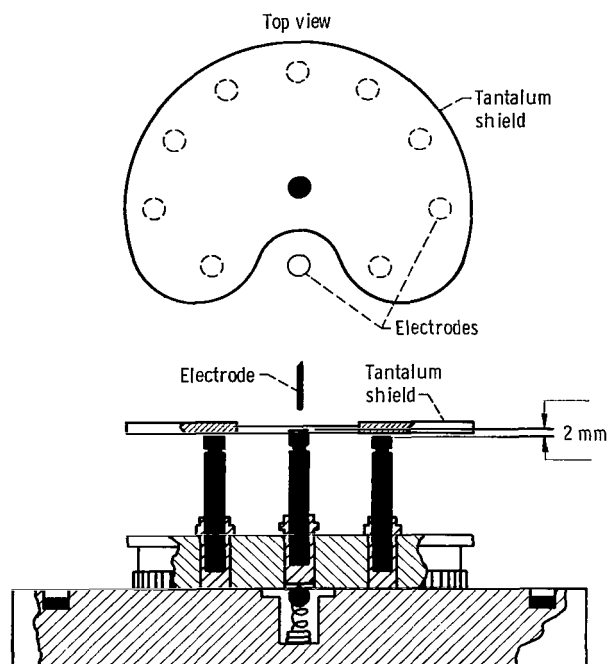


Figure 2. - Cross section of controlled atmosphere chamber showing tantalum shield and electrode positioning ball indent with electrode in raised position.

quartz cylinder on rubber gaskets fabricated from a Viton rubber compound. To operate the arc chamber at pressures above 760 torr, up to 7500 torr, additional clamping to that shown in figure 1 is necessary. This additional clamping was provided by compressing the steel plates shown in figure 1 between auxiliary aluminum plates, fitted with three toggle bolts, about 1 centimeter in diameter. The bolts were tightened symmetrically with a torque wrench to a torque of 60 inch-pounds. Also shown are facilities for loading up to 11 sample electrodes, which are sequentially arced by rotating a vacuum-sealed shaft and gear arrangement. A graphite counter electrode is held by an expansible bellows assembly, which permits control of the analytical gap space and replacement of the electrode. The tantalum cover plate shown protects electrodes not in arcing position and minimizes effects of cross contamination.

Because the tantalum shield and auxiliary electrodes are located between the analytical gap and the spectrographic slit, features that aid in optical alignment and prevent vignetting are noteworthy. First, the tantalum shield was grooved along the light path to about a 0.5 millimeter thickness as shown in figure 2. Secondly, the figure also shows a mechanism to raise the sample electrode 2 millimeters as it revolves into arcing position. A spring-loaded steel ball provides the vertical movement and may also be used as

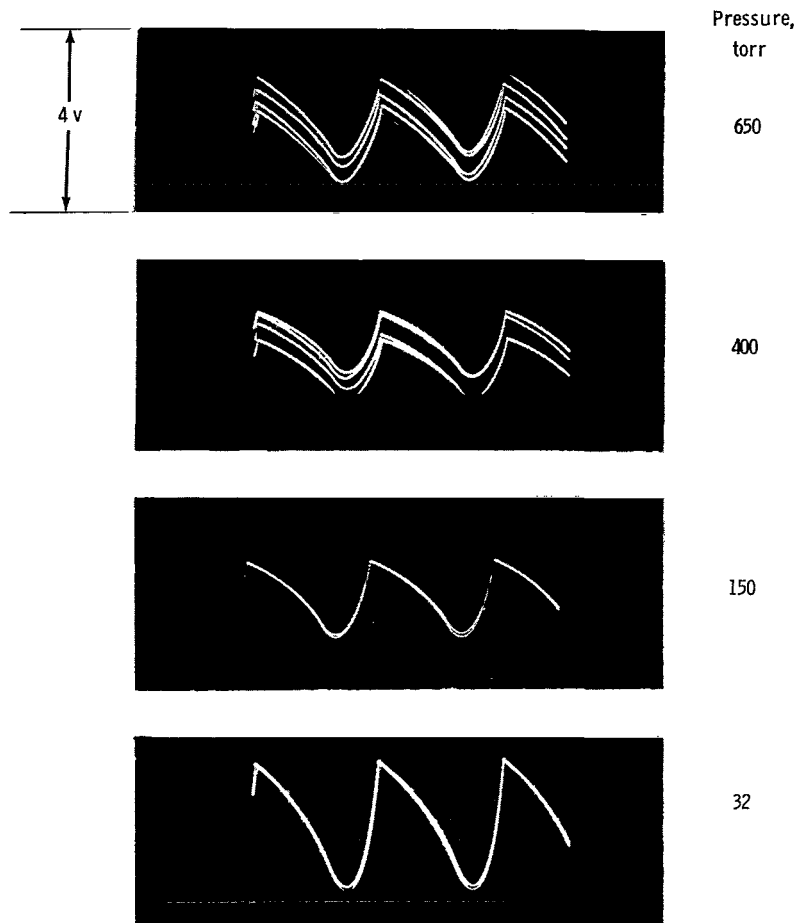


Figure 3. - Oscillographic recording of voltage across analytical gap showing improved electrical stability of argon arc at reduced pressure. Graphite electrodes; 30-ampere direct-current arc.

a positioning indent. With this mechanism the sample electrode is positioned vertically to within 1 millimeter of the optical solid angle.

The chamber, which may be repeatedly evacuated, is connected to a vacuum system capable of reducing the pressure from 750 to  $10^{-3}$  torr in 1 minute. The chamber is mounted in tandem with a conventional arc-spark stand using a three-lens optical system (ref. 12) with the external mask held between the jaws of the electrode clamps in the arc-spark stand. This arrangement permits excitation of samples in either air or argon atmospheres using the appropriate excitation stand.

## OBSERVATIONS OF ARC AT REDUCED PRESSURE

The free-running arc between graphite electrodes in a static argon atmosphere at

750 torr is unstable. Under these conditions an "anode-flame" as long as 5 centimeters develops at a 30-ampere current and revolves about the electrode axis when the electrodes are vertically oriented. This characteristic instability of the arc discharge is especially enhanced in rare gases where the vaporization of the graphite electrodes and the vapor density in the positive column is relatively low. Conversely, the discharge tends to become more stable when metal salts are vaporized from the anode.

Another factor that can affect the stability of the arc in argon is the pressure of the supporting atmosphere. As the pressure in the chamber is reduced, the positive column



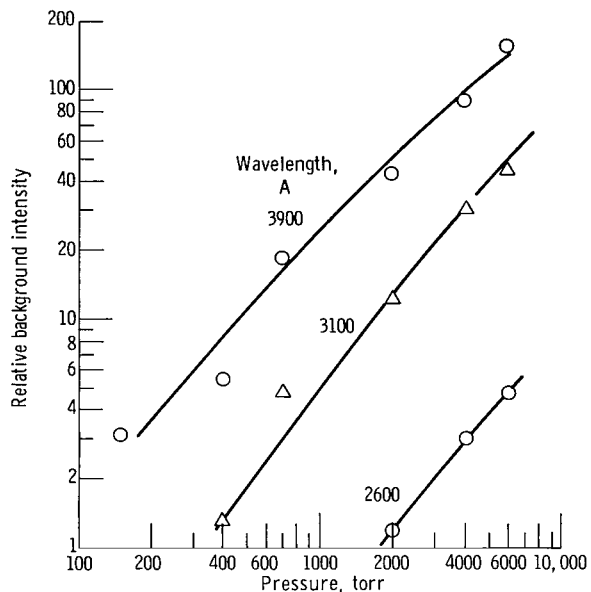


Figure 4. - Effect of reducing pressure of argon arc on background intensity. Graphite electrodes; 30-ampere arc.

increases in volume and the discharge becomes more stable. Figure 3 shows cathode ray oscillograms of the voltage fluctuations measured between the anode and cathode at various pressures. The improved electrical stability at lower pressures is apparent and correlates with the overall reduction of the lateral wandering of the positive column.

At reduced pressures the photometric brightness of the arc is diminished. Figure 4 is a plot of relative background intensity as a function of pressure that behaves as would be predicted from the visual brightness. The parallelism of the curves at the three wavelength positions serves to illustrate that the light distribution remains essentially unchanged over this wavelength region.

The overall excitation characteristics and temperature of the arc are also not greatly changed at moderate pressures

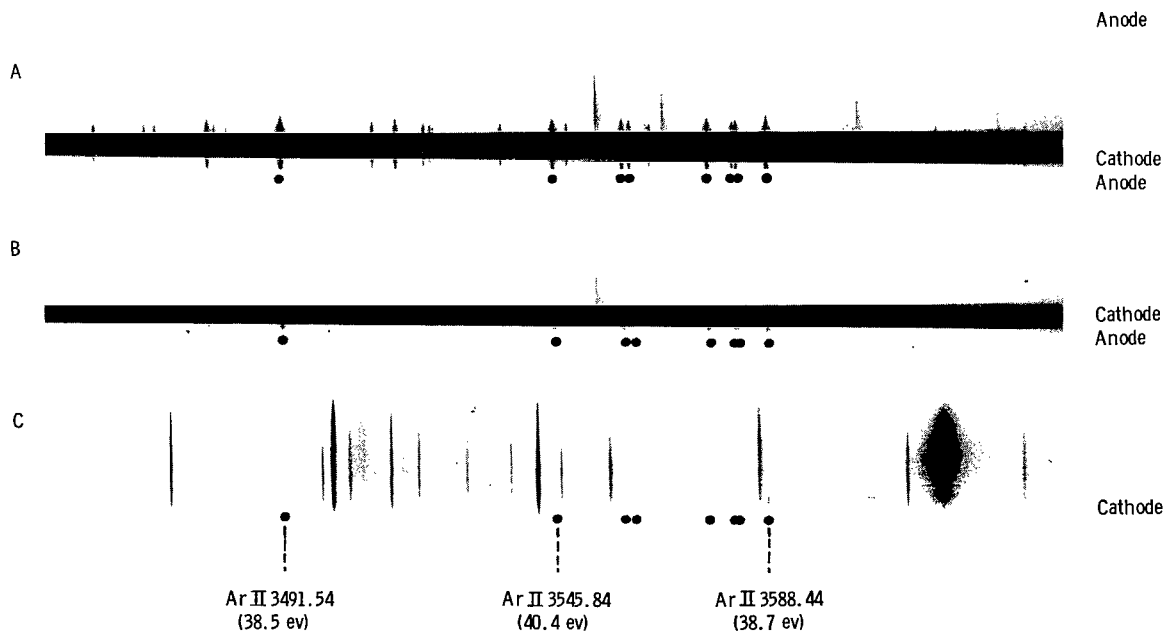


Figure 5. - Spectra with arc column focused on slit showing argon ion lines excited near cathode. A, spectra in argon at 200 torr; B, spectra in argon at 700 torr; C, spectra in argon at 200 torr using silver chloride buffer.

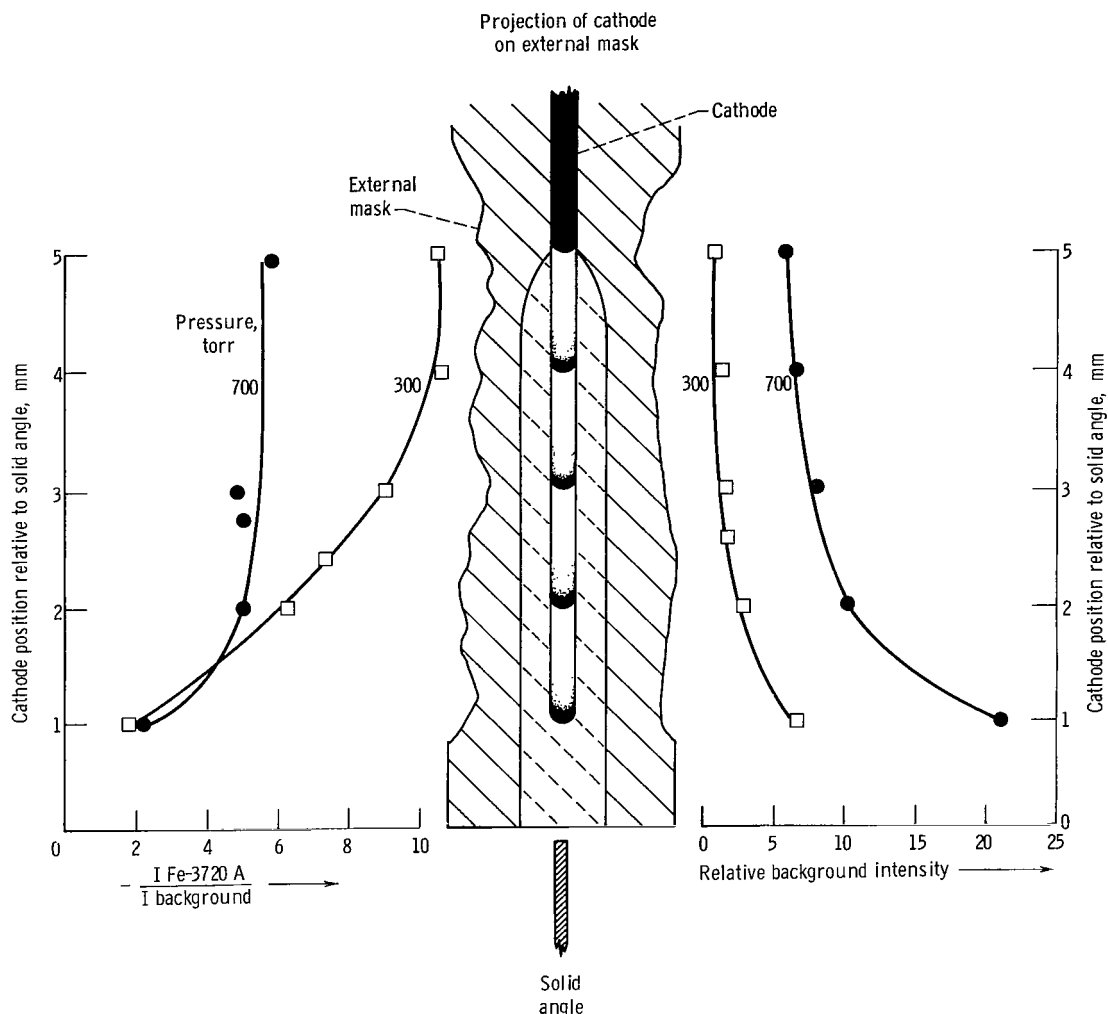


Figure 6. - Effect of masking cathode fall region of argon arc on line-to-background ratio of Fe-3720 Å and on background intensity at 3719 angstroms.

(ref. 13), although certain regions of excitation in the discharge may become more predominate. Figure 5 illustrates the enhancement of the cathode fall region at reduced pressure. The first spectrum shown is an arc between graphite electrodes at 150 torr with the arc focused on the slit. The lines marked are argon ion lines having excitation energies of about 39 electron volts (ref. 14). The second spectrum shows the same conditions except the pressure has been increased to 750 torr and the cathode fall region has receded toward the cathode. This enhancement of the cathode fall region at reduced pressures may be used to intensify excitation of elements, such as the halogens, whose atomic lines require higher energies for excitation. This effect was used by Professor V. A. Fassel and J. Tveekrem of Iowa State University of Science and Technology for the determination of fluorine. No cathode layer effect was observed for the neutral or singly ionized spectra of the common elements, and the effect was not useful for the determina-

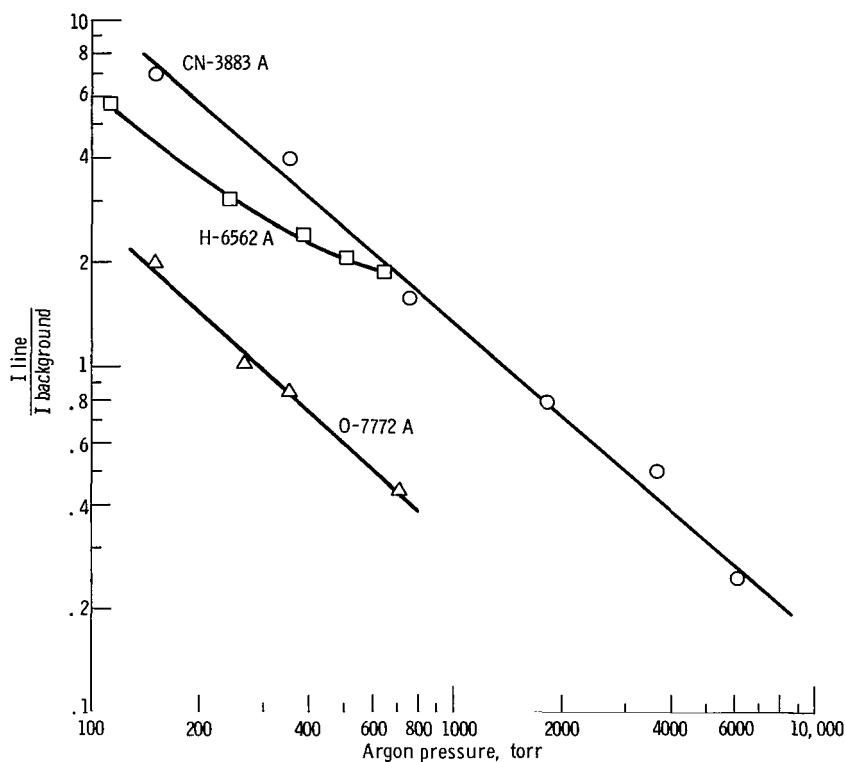


Figure 7. - Increase in line-to-background intensity ratios of gases in arc at reduced argon pressure. Data for H-6562 A derived from reference 15 (p. 242).

tion of these elements. For the determination of the common elements, however, masking the emission from this region of the arc column decreases the background and improves line-to-background ratios. Figure 6 shows the effect of masking this cathode region on line-to-background ratios. The illustration in the center of the figure represents the optical image of the cathode as projected on the external mask. On the left is a plot showing the effect of masking on the intensity ratio of Fe-3720 A at 300 and 700 torr. The plot on the right shows the effect of masking on the relative background intensity also at 300 and 700 torr. Each increment that the image of the cathode is moved away from the edge of the external diaphragm diminishes the background and improves the line-to-background ratio. The numbers on the ordinate represent actual distances from the solid angle in the analytical gap.

By the simple expedient of reducing the arc pressure and by properly masking the cathode, the line-to-background ratios will be enhanced provided the emission of atomic lines is not diminished. An example of such a result is shown in figure 7. The effect of lowering the arcing pressure is to increase the line-to-background ratios when measuring oxygen, hydrogen, and nitrogen (as cyanogen) according to the technique described in reference 15. In applying this procedure to trace elements in highly pure materials, the conditions are not so ideal as in the case of these permanent gases. Metal atoms, of

course, have a relatively short lifetime in the discharge since they diffuse out and are immediately deposited in the cooler zones of the apparatus. To take advantage of the lower background intensity at reduced pressure it is necessary to consider the means of introducing the sample atoms into the discharge, as well as their excitation. Thus, the line intensity will be determined not only by the excitation con-

ditions but also by the equilibrium population of impurity atoms entering the positive column and those leaving by diffusion out of the gap.

In the direct-current arc the sample enters the gap by thermal vaporization with or without chemical changes. The effect of pressure on electrode temperature is therefore of interest. Figure 8 shows that the optical electrode temperature and presumably, therefore, the vaporization of the sample are dependent only on the current, as might be expected. By reducing the pressure, therefore, the current density in the column may be reduced without disturbing the temperature of the electrode furnace. It should be mentioned, however, that since these data were obtained by optical pyrometry, they would not reveal localized temperature gradients.

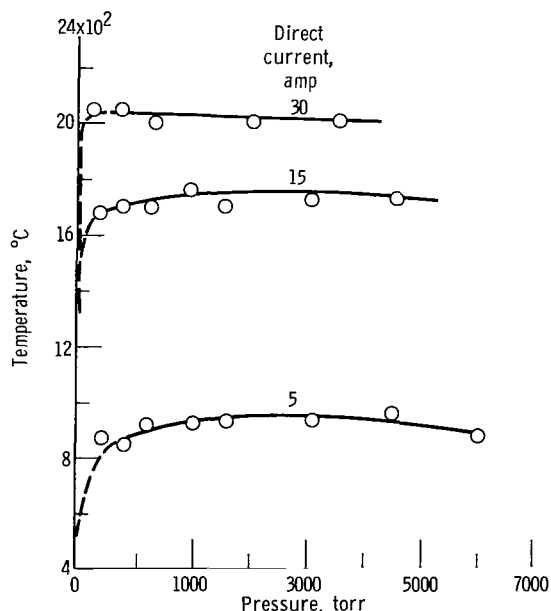


Figure 8. - Average anode temperature in argon as function of current and pressure.

Such gradients may occur on the top of the anode because of the effect of pressure on the anode spot size. At the lower pressures shown the electrode temperature falls off rapidly as indicated by the dotted line. This is caused by the energy being lost as the expanded discharge contacts the walls of the vessel.

The effective excitation temperature that is determined predominantly by the metastable states of argon (about 11 ev) is not conducive to the efficient excitation of the sensitive neutral atom lines of the common elements (3 to 6 ev). Ion lines, while more suitable from this standpoint, do not show significant enhancement compared to the neutral atom lines in air with a few notable exceptions. The excitation temperature of the arc in argon may be reduced to conform more closely to the requirements for neutral atom lines by flooding the gap with metal atoms of low ionization potential. The cooling effect of silver atoms on the argon arc is evidenced by the decreased intensity of the cathode fall region as shown in the third spectrum of figure 5. By following this procedure it was found that the excitation effect could be achieved in argon using the common carrier salts

TABLE I. - SUMMARY OF EXPERIMENTAL CONDITIONS

Instrument	Jarrell-Ash, 3.4 m, Ebert mount Grating, 1200 lines/mm Camera, 76 cm
Slit width	30 microns
Spectral dispersion	2.5 Å/mm
Wavelength	2500 to 4200 Å
Excitation	Rectified direct-current arc in argon Sample, cathode
Electrodes	Anode, 13.2-mm diam., graphite Cathode, 4.8-mm diam., graphite, cupped (Ultra Carbon Corporation, 105-S; National Carbon Co., L-3906)
Sample	30 microliters of dilute solutions of metal chlorides and 2 mg of AgCl added to each electrode
Analytical gap	11 mm total, position optical solid angle as described, 3 mm in height, to within 1 mm of anode
External optics	Three-lens external diaphragm (ref. 12)
Exposure time	20 sec (no prearc)
Emulsion	Kodak SA 3

including silver chloride (AgCl), gallium sesquioxide ( $\text{Ga}_2\text{O}_3$ ), and indium sesquioxide ( $\text{In}_2\text{O}_3$ ). The enhancements have also been observed by using buffers that are not usually associated with carrier distillation such as silver oxide and silver metal. The mechanisms by which these enhancements occur are discussed in reference 16. In the presence of these salts the emission spectrum of neutral atom lines is greatly enhanced, while the pressure of the supporting argon can be reduced without detrimentally affecting either the line intensity or the electrode temperature. Since the background was reduced under these conditions, the line-to-background ratios were improved.

## RESULTS

A pressure variation study, using the experimental parameters of table I, for typical elements is shown in figure 9. These curves, in addition to showing good absolute sensitivity, exhibit a broad maximum at pressures reduced from atmospheric. On the basis of this data an arcing pressure of 350 torr was adopted to complete table II of absolute sensitivities. Also shown in table II is a list of sensitivities obtained by the hollow cathode and

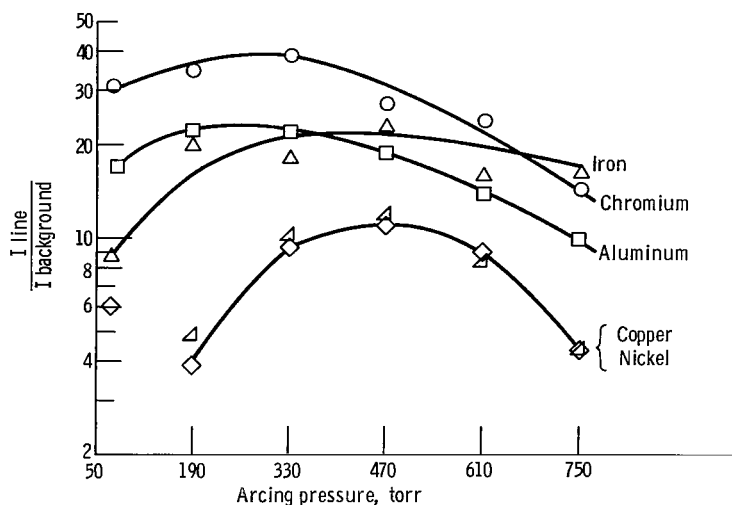


Figure 9. - Effect of arcing pressure on line-to-background intensity ratios of typical elements when arced in presence of silver chloride. Weight of elements,  $5 \times 10^{-8}$  gram.

copper spark procedures (ref. 17). The reported conditions for the hollow cathode were 1100 to 1500 milliamperes in a helium carrier gas. The cathode was waterproofed with polystyrene solution. No attempt was made to pretreat the electrodes for the direct-current arc in argon. Experimental conditions in argon other than pressure were optimized for iron, and this element yields a higher apparent sensitivity under these conditions. Those elements reported less than indicate that under these conditions the background could not be measured, and the line-to-background ratio is therefore limited by the total light on the photographic plate. In most cases the numbers compare favorably with the hollow cathode data. It is important to note, however, that quantitative comparisons cannot be made from these data since they were obtained from instruments having different characteristics. The data for argon - silver chloride were obtained at a dispersion of 2.5 angstroms per millimeter, and the hollow cathode and copper spark data were obtained from an instrument the dispersion of which was not known to the author. The criteria for limits of detection were a line intensity 30 percent over background in the case of argon - silver chloride and 5 to 10 percent over background for the remaining data.

## DISCUSSION AND SUMMARY

The application of a controlled-atmosphere system, as described, is believed to constitute a new general approach to trace analysis. In preliminary experiments with volatile or refractory matrices including sodium chloride, tungsten metal, and mixtures of tungsten metal and uranium oxides, line-to-background enhancements were observed for

TABLE II. - COMPARISON OF ABSOLUTE SENSITIVITIES

Element	Silver-buffered argon arc at 350 torr, g	Hollow cathode (a)	Copper spark (a)
Aluminum	$1.5 \times 10^{-9}$	10 <sup>+</sup>	10
Silver	-----	.03	5
Boron	-----	1	1
Beryllium	.12	.03	.2
Cadmium	<20	30	200
Cobalt	4	.3	50
Chromium	2	1	5
Copper	.4	.03	-----
Iron	.3	3	50
Gallium	10	.03	100
Potassium	<20	10	10
Lithium	<1	.1	.2
Magnesium	.2	.03	1 <sup>+</sup>
Manganese	1.3	.03	2
Sodium	<7	.03	10 <sup>+</sup>
Nickel	3	1	10
Phosphorus	30	30	2000
Lead	1	10	5
Antimony	2	100	500
Silicon	3	1	10
Tin	7	10	-----
Zinc	45	3	200
Molybdenum	1.6	-----	-----
Titanium	2.0	-----	-----

<sup>a</sup>Ref. 17.

all elements sought. Calibration curves for trace elements in silver chloride are linear down to 1 to 10 parts per billion for copper, iron, aluminum, chromium, titanium, magnesium, calcium, and silicon.

These enhancements are caused by the cumulative effects of several mechanisms. Some of these phenomena will be recognized as the principal mechanisms for spectrographic methods reported in the literature. For example, the use of nitrogen-free atmospheres to suppress cyanogen and to permit the use of the more sensitive elemental lines has become common practice in many laboratories. A fact not equally well recognized, however, is the further improvement in the analytical system, with respect to background radiation, when using a gas-tight chamber in which the discharge takes place in relatively pure noble gases. Under such conditions the intensity of the continuous background, as well as the cyanogen band intensities, are markedly reduced compared to flowing gas

systems that are partially open to the atmosphere. If in addition the chamber is vacuum tight, the arcing pressure may be optimized to further reduce the continuous background. Line radiation is also sharper at reduced pressure because the line broadening effects are reduced. For the experimental conditions reported, the atomic line intensities also decrease when the discharge pressure is reduced to about 350 torr, but to a lesser degree than the continuous background. At still lower pressures the line intensities diminish at a greater rate than the background, resulting in a maximum in the line-to-background ratios. The explanation for these observations is not clear at this time. Since neutral atom lines and ion lines behave similarly, the phenomenon is probably related to kinetic processes, such as diffusion, rather than excitation processes per se.

It is interesting to note that this technique permits the current density in the positive column to be changed independently of the electrode temperature by varying the pressure of the supporting atmosphere. In the conventional arc in air the current density is reduced by lowering the current, and the electrode temperature is controlled by means of electrode geometry. Thus, it would appear that in the pressure-tight system the analyst is provided with a degree of freedom by which he may uniquely control the vaporization of the sample. For refractory matrices the strong development of selective volatilization is a contributing factor toward the attainment of high line-to-background ratios. The use of atmospheres with negligible reactivity is in principle similar to the addition of graphite to the sample to suppress volatilization of the matrix.

The advantageous use of these effects in analytical spectrochemistry requires, ideally, that the supporting atmosphere be chemically inert and at the same time provide an environment favorable for the production of neutral atom lines. These are, apparently, conditions that are mutually incompatible because the noble gases, which satisfy the first criterion, preferentially excite the ion spectra of the impurities, which violates the second criterion. All of the described effects, however, operate in favor of high line-to-background ratios when metal ions having low excitation potentials are vaporized into the arc column.

Although the procedural aspects of this technique are similar to the carrier distillation method described in reference 18, the primary mechanism for the line enhancements reported here is not dependent on intimate contact between the buffer salt and the sample. This is evidenced by the fact that the line enhancements occur when the buffer salt and samples are vaporized from opposite electrodes and also when the buffer salt and sample are placed in separate cavities in the same electrode. Generally, vaporization from the cathode results in lower background and is therefore the preferred approach. When the buffer salt is introduced from the same electrode as the sample, however, there remains the possibility that the enhancements due to excitation effects and those due to distillation phenomena will operate simultaneously.

These excitation enhancements can be ascribed to the temperature dependence of the



atomic line emission in the argon arc. The data reported in this work substantiate the conclusion, which was drawn by other workers (ref. 16), that the carrier effect is often due to these temperature effects. Although the temperature of the silver-buffered argon arc has not been measured, nor has it been established that the condition of thermal equilibrium exists, it is probable that the arc temperature is still higher than is desirable for the most efficient excitation of neutral atom lines. As a case in point, the MgII 2802 to MgI 2852 intensity ratio is about 7 in the arc described here, whereas in a copper arc at 5100<sup>0</sup> K (ref. 19) this ratio is 0.1 (ref. 20). Some other ion lines having higher intensities than neutral atom lines in our arc can be found in table III. It is possible that the use of other buffering salts will result in further improvement in detection

TABLE III. - ELEMENTS HAVING ION  
LINE AS MOST SENSITIVE LINE IN  
SILVER-BUFFERED ARGON ARC

Element	Wavelength, $\lambda$ , A	Total excitation energy, ev
CaII	3933.67	9.2
BeII	3130.42	13.2
MgII	2795.53	12.0
TiII	3349.41	11.1
TaII	2965.13	12.0
ZrII	3391.97	10.8

limits over those reported here. Nevertheless, the method for obtaining high sensitivity reported here demonstrates the usefulness of temperature adjustments in the arc column for analytical purposes.

In the application of these procedures to trace and microanalytical problems, the inherent blank of the system must be considered as a source of noise in addition to the spectral noise. It is not uncommon in analytical procedures that because of a high blank the limits of determination are orders of magnitude higher than the smallest signal that can be measured by the de-

tecting system. The blank originating from even the highest purity electrodes is effectively reduced by preconditioning the sample electrodes by arcing in argon at 30 amperes. In addition, trace elements originating from the graphite electrodes are minimized because the gasification of the graphite in argon is negligible. For example, when 3/16-inch-diameter electrodes were arced for 12 minutes at 30 amperes, the weight loss of the electrodes was less than 1 milligram. This represents a small fraction of the weight loss when compared with the same conditions in air. A source of blank in this system when applying this technique to analysis of pure materials is the residual impurities in the carrier salt. When silver chloride is used as a buffer, only a few milligrams are used for a 1-gram sample. The blank from this quantity of carrier-grade silver chloride is negligible when measuring trace elements in the fractional parts-per-million range.

Lewis Research Center,  
National Aeronautics and Space Administration,  
Cleveland, Ohio, November 5, 1964.

## REFERENCES

1. Auger, Pierre.: Current Trends in Scientific Research. United Nations Educational, Scientific and Cultural Organization (Paris), 1961.
2. Adelstein, S. J.; and Vallee, B. L.: The Effect of Argon Atmospheres on the Intensity of Certain Spectral Lines. *Spectrochim. Acta*, vol. 6, 1954, pp. 134-138.
3. Vallee, Bert L.; and Peattie, Ruth W.: Volatilization Rates of Elements in the Helium Direct Current Arc. *Analytical Chem.*, vol. 24, no. 3, Mar. 1952, pp. 434-444.
4. Rupp, Richard L.; Klecak, George L.; and Morrison, George H.: Spectrographic Analysis of High Purity Nickel. *Analytical Chem.*, vol. 32, no. 8, July 1960, pp. 931-933.
5. Morrison, George H.; Rupp, Richard L.; and Klecak, George L.: Spectrographic Analysis of High Purity Silicon Carbide. *Analytical Chem.*, vol. 32, no. 8, July 1960, pp. 933-935.
6. Zhiglinskii, A. G.; Zaidel, A. N.; and Karklina, E. A.: Study of a Direct Current Arc at Increased Pressure. *Optics and Spectroscopy*, vol. 10, no. 6, June 1961, pp. 368-370.
7. Zakharov, V. P.: Effect of the Composition and Pressure of the Atmosphere on the Entry of Atoms of Certain Elements from the Electrodes of an Arc Discharge. *Izvest. Vysshikh Ucheb. Zavedenii Fiz.*, no. 4, 1961, pp. 92-95.
8. Kaiser, H.: The Calculation of the Sensitivity of Detection in Spectrochemical Analysis. *Spectrochim. Acta*, vol. 3, 1947, pp. 40-67.
9. Mandelstam, S. L.; and Nedler, V. V.: On the Sensitivity of Emission Spectrochemical Analysis. *Spectrochim. Acta*, vol. 17, 1961, pp. 885-894.
10. Nedler, V. V.; and Arakel'yan, N. A.: Problems in the Analysis of Highly Pure Metals, *Zavodsk. Lab.*, vol. 28, 1962, pp. 672-674.
11. Evens, F. Monte; and Fassel, Velmer A.: Emission Spectrometric Determination of Oxygen in Niobium Metal. *Analytical Chem.*, vol. 33, no. 8, July 1961, pp. 1056-1059.
12. Feldman, C.; and Ellenburg, J. Y.: Contrast Changes of Eastman Kodak Spectrum Analysis No. 1 Emulsion During Cold Storage and Their Effect on Observed Intensity Ratios. *Spectrochim. Acta*, vol. 7, 1956, pp. 349-357.
13. Semenova, O. P.; and Kokhanenko, V. V.: Mechanism of the Excitation of Spectral Lines in a Low-Pressure Arc Discharge. *Akad. Nauk. Izvest. Ser. Fiz.*, vol. 14, 1950, pp. 727-731.

14. Zaidel', A. N.; Prokof'ev, V. K.; and Raiskii, S. M.: Tables of Spectrum Lines. Pergamon Press, 1961.
15. Fassel, V. A.; Gordon, W. A.; and Jaskinskii, R. J.: Spectrographic Determination of Oxygen, Nitrogen and Hydrogen in Metals. Prog. in Nuclear Energy - Analytical Chem., Pergamon Press, 1959, p. 230.
16. Samsonova, Z. N.: On the Mechanism of the "Carrier" Effect on the Intensity of Spectral Lines. Optics and Spectroscopy, vol. 12, no. 4, Apr. 1962, pp. 257-261.
17. Korovin, Yu. I.: Increasing the Sensitivity of Determinations by Means of Discharge in a Hollow Cathode. Zhur. Analiticheskoi Khim., vol. 16, 1961, pp. 494-495.
18. Scribner, Bourdon F.; and Mullin, Harold R.: Carrier-Distillation Method for Spectrographic Analysis and Its Application to the Analysis of Uranium-Base Materials. J. Res. Natl. Bur. Std. vol. 37, no. 6, Dec. 1946, pp. 379-389.
19. Corliss, Charles H.: Temperature of a Copper Arc. J. Res. Natl. Bur. Std. vol. 66A, no. 1, Jan. -Feb. 1962, pp. 5-12.
20. Meggers, W. F.; Corliss, C. H.; and Scribner, Bourdon F.: Tables of Spectral-Line Intensities. Monograph 32 - Pt. I, NBS, Dec. 1961.

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